

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
28 November 2002 (28.11.2002)

PCT

(10) International Publication Number
WO 02/095847 A1

- (51) International Patent Classification⁷: H01M 2/16
- (74) Agent: **BERSON, Bennett, J.**; Quarles & Brady LLP, P.O. Box 2113, Madison, WI 53701-2113 (US).
- (21) International Application Number: PCT/US02/16823
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 24 May 2002 (24.05.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/293,588 24 May 2001 (24.05.2001) US
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant: **RAYOVAC CORPORATION** [US/US]; 601 Rayovac Drive, Madison, WI 53711 (US).
- (72) Inventors: **BUSHONG, William, C.**; 6306 Keelson Drive, Madison, WI 53705 (US). **CURTIS, Stephanie, R.**; 412 Schwantz Road, Pardeeville, WI 53954 (US). **DAVIDSON, Gregory, J.**; 323 South Main Street, Oregon, WI 53575 (US). **MIHARA, David, R.**; 5 San Antonio Court, Madison, WI 53719 (US). **MOY, Gregory, S.**; 5301 Shawano Terrace, Madison, WI 53705 (US). **NDZEBET, Ernest**; 8501 Old Sauk Road, Apartment 228, Middleton, WI 53562 (US). **ROOT, Michael, J.**; 585 Arthur Street, Verona, WI 53593 (US). **VU, Viet, H.**; 3926 Meridian Circle, Verona, WI 53593 (US).
- Published:**
- with international search report
 - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: CONFORMAL SEPARATOR FOR AN ELECTROCHEMICAL CELL COMPRISING A CROSSLINKED POLYMER

(57) Abstract: An electrochemical cell is presented having an improved separator disposed at the interfaced of the anode and cathode. In particular, the separator conforms to the contour of the electrode and is thinner than conventional separators made of non-woven fabric. The conformal separator may be formed from combinations of certain polymers and inorganic crosslinking agents. Preferably, the crosslinking agent is a borate or boric acid derivative, and the polymer preferably comprises poly vinyl alcohol.

BEST AVAILABLE COPY

CONFORMAL SEPARATOR FOR AN
ELECTROCHEMICAL CELL COMPRISING A
CROSSLINKED POLYMER.

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. provisional patent application No. 60/293,588 entitled "Conformal Separator for an Electrochemical Cell" and filed May 24, 2001, the disclosure of which is hereby incorporated by reference as if set forth in its entirety herein.

STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH OR DEVELOPMENT

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of Contract No. CECOM DAAB07-00-C-D301.

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to electrochemical cells, and in particular, relates to an improved conformal separator usable in zinc air and alkaline cells and further relates to methods to apply such separators.

Description of the Related Art.

[0002] Conventional electrochemical cells, such as alkaline cells, comprise a cathode which is a mixture of manganese dioxide, MnO_2 , and a carbonaceous material, typically graphite. In some cylindrical alkaline cells, this cathode mixture, which is often wetted with an alkaline electrolyte, is compressed into annular rings. The cathode is then placed into a metal container, which then serves as the positive current collector. An anode, which generally comprises a powdered zinc disposed in a gel, such as carboxymethylcellulose, is also placed into the metal container. A negative current collector, usually a brass pin or nail, is placed in electrical contact with the anode.

[0003] In order for the cell to operate, electrolyte must transfer between the anode and cathode. However, the anode and cathode must be electrically isolated, otherwise a short

circuit will cause the open circuit voltage of the cell to decrease rapidly, thereby causing the cell to fail prematurely. The electrolyte transfer and electrical isolation are conventionally achieved using an annular separator that is disposed at the interface between the anode and cathode. Separators typically comprise a non-woven, inert fabric that has sufficient porosity to enable permeability to gas and liquid such as an electrolyte, but substantially solid so as to prevent the cathode from electrically shorting with the anode. The fabric is typically greater than 0.2 mm thick and often more than one layer is required. Accordingly, the separator occupies significant volume within the cell that could otherwise be occupied by active cell ingredients, which would result in greater performance by the cell. However, fabrics of lesser thickness are susceptible to tearing and are thus impractical for use during fabrication of the cell. What has been historically needed therefore is a separator that achieves electrical isolation while permitting electrolyte transfer and that occupies as little volume within the cell as possible.

[0004] One method used to overcome the limitations of sheet separators is to apply a material or mixture of materials in a carrier directly to the electrodes of an electrochemical cell. The resulting compound thus conforms to the shape of the electrode, thus eliminating air pockets that are associated with annular cloth separators, and is additionally thinner than cloth separators. Accordingly, more internal volume may be occupied by active cell ingredients.

[0005] Currently, these compounds may comprise cellulose fibers and soluble cellulose polymers disposed in a solvent carrier. Other methods use a copolymer with a plasticizer onto an electrode element to produce a separator film. Still other methods apply a suspension of inorganic material in a carrier containing a polymer binder. One significant disadvantage of these methods is the carrier solvents or plasticizers which must be removed or displaced with electrolyte in order to produce a functioning separator film that facilitates electrolyte transfer.

[0006] Yet other known methods use a polymer coating that is applied to the electrode to form the separator. However, these polymers must be cured or solidified in some manner, such as by allowing a polymer solution with a high melting point to cool or drying the polymer solution, both of which consume time and resources, thereby creating inefficiencies in the fabrication process. Alternatively, polymerization is achieved by combining monomers or oligomers with a polymerization initiator and exposing the mixture to heat or a radiation source, such as ultraviolet light or γ -radiation, thereby also

creating inefficiencies. Alternatively, crosslinking is currently accomplished using an organic cross linking agent that creates a solid polymer film. However, organic crosslinking agents, such as divinyl sulfone, are toxic and hazardous to handle.

[0007] What is therefore needed is an improved separator for an electrochemical cell that conforms to the electrode and that is nontoxic and efficient to manufacture, thus avoiding the disadvantages associated with current methods.

BRIEF SUMMARY OF THE INVENTION

The present invention provides an electrochemical cell that includes a container, a cathode material disposed in the container, an anode material disposed in the container; and a conformal separator disposed between the anode and cathode that provides electrical isolation between the anode and cathode while permitting electrolyte transfer between the anode and cathode, the separator being formed from a polymer and an inorganic crosslinking agent.

[0008] This and other aspects of the invention are not intended to define the scope of the invention for which purpose claims are provided. In the following description, reference is made to the accompanying drawings, which form a part hereof, and in which there is shown by way of illustration, and not limitation, preferred embodiments of the invention. Such embodiments do not define the scope of the invention and reference must be made therefore to the claims for this purpose.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Reference is hereby made to the following figures in which like reference numerals correspond to like elements throughout, and in which:

[0010] Fig. 1 is a sectional side elevation view of a cylindrical electrochemical cell having a separator constructed in accordance with the preferred embodiment;

[0011] Fig. 2 is a sectional side elevation view of a metal-air cell having a separator constructed in accordance with the preferred embodiment;

[0012] Fig. 3 illustrates the discharge profile of size "AA" cells having a separator constructed in accordance with the preferred embodiment compared to conventional cells having a separator made of non-woven fabric; and

[0013] Fig. 4 illustrates the discharge profile of size "AA" cells having a conformal separator applied to a traditional non-woven fabric in accordance with an alternate

embodiment compared to conventional cells having a separator made solely of non-woven fabric.

[0014] DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0015] Referring initially to Fig. 1, a cylindrical cell constructed in accordance with a preferred embodiment of the present invention is illustrated having a positive terminal 21, a negative terminal 23, and a positive current collector in the form of an unplated cylindrical steel container 20. Container 20 is initially closed at its end proximal the positive terminal 21 and open at its end proximal the negative terminal 23 such that the negative end of container is crimped to close the cell as is understood generally by a skilled artisan. At least one or more cylindrical annular cathode rings 24, formed such that their outside diameters at their outer peripheral sidewalls are greater than the inside diameter of the positive current collector 20, are forced into the positive current collector. A coating 22, preferably carbon, is applied to the radially inner surface of container 20 to enhance the electrical contact between the cathode rings 24 and the container. Installation of the cathode rings 24 forms a pressure contact with the coating 22. Cathode rings 24 further have radially inner walls that form a centrally shaped void 28 within which anode 26 is disposed.

[0016] A bead 30 is rolled into the container near the open end to support a sealing disk 34 as will be described below. Anode 26, which is placed inside of the cathode rings 24, is generally cylindrically shaped, and has an outer peripheral surface which engages the inner surfaces of a separator 32, and comprises gelled zinc in accordance with the preferred embodiment.

[0017] The sealing disk 34, having a negative current collector 36 extending therethrough, is placed into the open end of the container 20 and in contact with the bead 30. The open end of the container 20 is crimped over the sealing disk 34 thus compressing it between the crimp and the bead 30 to close and seal the cell. An insulation washer 38 with a central aperture is placed over the crimped end of the cell such that the end of the negative current collector 36 protrudes through the aperture. A contact spring 40 is affixed to the end of the negative current collector 36. Negative terminal cap 42 and positive terminal cap 44 are placed into contact with the contact spring 40 and the positive current collector 20, respectively, and an insulating tube 46 and steel shell 48 are placed around the cell and crimped on their ends to hold the terminal caps in place. It should be appreciated that steel shell 48 and insulating tube 46 could be

eliminated to increase the internal volume for the cell that may be occupied by active ingredients. Such an arrangement is described in U.S. Patent No. 5,814,419 assigned to Rayovac Corporation, the disclosure of which is hereby incorporated by reference herein for the purposes of background information. Rayovac primary alkaline cells having no steel shell 48 or insulating tube 46 are commercially identified as LR20 (size "D") and LR14 (size C) type cells.

[0018] Separator 32 is most preferably an ionically permeable separator, and is interposed between anode 26 and the inner peripheral sidewalls of cathode rings 24 to prevent electrical contact between the anode and cathode while permitting ionic transport between anode 26 and the cathode 24. Separator further extends radially across the cell proximal the positive end and between the inner surface of the can 20 and the anode 26. An alkaline aqueous electrolyte typically comprising potassium hydroxide and water at least partially wets anode 26, cathode rings 24, and separator 32. Unlike separators of conventional cells, separator 32 is advantageously a conformal separator formed from a polymer mixed with an inorganic crosslinking agent that occupies significantly less volume than a conventional fabric, thereby providing greater volume for active material, as will be described in more detail below.

[0019] Referring to Fig. 2, a button-size metal-air cell 50, also constructed in accordance with the preferred embodiment, includes a negative electrode 52 (anode), and corresponding anode can 54 having an electrolyte with anode material 46 disposed therein. In accordance with the preferred embodiment, the anode material comprises beryllium copper, though it should be easily understood by one having ordinary skill in the art that any well known anode material could be used, such as tri-clad copper-steel-nickel, stainless steel, copper, nickel, or a combination thereof.

[0020] Anode can 54 has a top wall 58, and an annular side wall 60 extending axially downwardly from its periphery. Top wall 58 includes an inner surface 62 and outer surface 64. Side wall 60 has an inner surface 72 and an outer surface 74, and further includes an edge region 76 remote from top wall 58, and intermediate region 78 between edge region 76 and top wall 58. An upper region 61 is disposed between top wall 58 and intermediate region 78, and prevents a beveled surface with respect thereto. Edge region 76 is generally defined as that portion of side wall 60 which is displaced radially inwardly of, and axially downstream of, region 78. Remote region 76 terminates at a distal end 80, which is located at the bottom edge of side wall 60. Side wall 60 presents a beveled edge at region 76 that joins region 78 to distal end 80, which extends axially upstream

therefrom. Top wall 58 and side wall 60 collectively define an open cavity 82 that contains the anode material 56.

[0021] The cell further includes a positive electrode (cathode 84), that is defined by a cathode assembly 86, including a cathode mixture and current collector that is contained within a cathode can 88 to enclose cavity 82. Cathode can 88 comprises nickel plated steel in accordance with the preferred embodiment, and has a bottom 90, and an annular side wall 92 extending axially upwardly from bottom 90. Side wall extends past the remote region 76 of anode side wall 60 so as to produce an outer structure that enables the cell to be inserted into conventional button cell cavities for use. Annular side wall 92 defines an upper beveled edge 93 that mates with the upper region of anode can 54. Side wall 92 includes an outer surface 102 and an inner surface 100 that faces outer surface 74 of anode can 54. A plurality of air ports 94 extend through bottom 90 of the cathode can, thereby providing avenues for the transport of oxygen into the cell adjacent the cathode assembly 86. An air reservoir 96 spaces the cathode assembly 86 from the bottom 90 and the corresponding ports 94. A porous air diffusion layer 98 fills the air reservoir 96, and comprises Teflon in accordance with the preferred embodiment. It should be appreciated that layer 98 may either be independent of, or integral with, the cathode assembly 86. The cathode 84 presents a surface that interfaces with the anode 52.

[0022] An insulating member 73 is disposed between the inner surface 70 of side wall 62 and outer surface 44 of side wall 30 at the intermediate region 48 and upper region 31 to provide electrical isolation between the anode can 24 and cathode can 58. In particular, insulator 73 is disposed axially upstream of the remote edge region, where the side walls 30 and 62 are in close proximity so as to require electrical isolation. Insulator 73 may comprise any suitable material well known in the art, such as propylene, cellulose, paper, waxed paper, or could comprise Teflon that is applied to the outer surface 44 of side wall 30, or inner surface 70 of side wall 62 to form a coating thereon. Insulator 73 has a small thickness, thereby permitting an increased volume for active material within container 52 as compared to conventional button cells.

[0023] The cathode 54 and anode 52 are further electrically isolated from one another via a radially compressed seal (hereinafter also referred to as "radial seal") that is disposed proximal the remote edge region 46. The seal extends substantially along the side wall of the anode can at the remote region 46 to further prevent leakage of electrolyte. The seal is accomplished via an insulating gasket 74 that comprises nylon 6,6 in accordance with

the preferred embodiment, but could alternatively comprise other suitable materials that are capable of providing the requisite insulation as well as the seal.

[0024] A separator 91 is disposed at the interface between the anode 52 and the anode-facing surface of cathode assembly 86. Separator 91 permits electrolyte transfer therebetween while providing electrical isolation therebetween. Separator 91 conventionally comprises a non-woven, inert fabric that has sufficient porosity to enable permeability to gas and liquid such as an electrolyte, but substantially solid so as to prevent the cathode from electrically shorting with the anode. In accordance with the preferred embodiment, separator 91 is a conformal separator formed from a polymer mixed with an inorganic crosslinking agent that occupies significantly less volume than a conventional fabric, thereby providing greater volume for active material.

[0025] It has been found as an unexpected result that separator 32 may be constructed in accordance with the preferred embodiment from specific combinations of certain polymers and inorganic crosslinking agents. In particular, these combinations may be sprayed onto or otherwise applied to coat the inner surface of cathode 24 to form the separator 32. The separator 32 has a reduced thickness when compared to traditional non-woven, inert fabrics and because the separator conforms to the electrode, any air pockets that might be present at the interface between the electrode and the fabric separator are eliminated. Accordingly, the conformal separator 32 occupies significantly less volume than traditional non-woven, inert fabrics, thereby permitting a greater amount of active material within the cell and improving the cell's performance. Additionally, the combinations employed in accordance with the preferred embodiment eliminate the need to use heat, light, radiation or hazardous organic crosslinking agents that are used in conventional methods for coating electrodes, as discussed above.

[0026] The construction of conformal separators 32 and 91 of the cylindrical cell and metal-air cell, respectively, may both constructed in accordance with the methods described below. In the description below, the present invention is described generally, followed by several examples of the formation and application of the conformal separator to the respective cathodes. It should be appreciated that, throughout the description, reference numerals are used that correspond to cell components of either the cylindrical cell or the metal-air cell. Such reference numerals are used for the purposes of clarity and convenience, and not to limit any particular embodiment of the present invention to the type of cell corresponding to the reference numerals used. Therefore, unless explicitly stated otherwise, the description below along with the following examples are applicable

to both cylindrical cells and metal-air cells. It should be further appreciated that while a skilled artisan may recognize the cylindrical cell illustrated in Fig. 1 as a size D cell, the present invention is applicable to any size cell, including but not exclusive to Size AAA, AA, C, D, and 9-Volt cells. The present invention is further applicable to any size metal-air cell including button cells.

[0027] In accordance with the present invention, when a crosslinkable polymer is mixed with an inorganic crosslinking agent (such as any borate derivative), a rapid reaction ensues and results in the production of a compound having properties suitable to prohibit electrical contact between the anode and cathode of an electrochemical cell while enabling ionic transport therebetween. In particular, a material containing a plurality of hydroxyl groups, such as a vinyl alcohol, and preferably a fully hydrolyzed polyvinyl alcohol (PVA) solution, is mixed with an inorganic solution containing a borate derivative. The ensuing rapid reaction produces borate-binding polyvinyl chains. In accordance with the preferred embodiment, the borate derivative, for example potassium borate, sodium borate, or zinc borate is crosslinked with polyvinyl alcohol that is at least partially hydrolyzed to render the compound insoluble in alkaline electrolyte.

[0028] The separator may be formed by first applying the crosslinking agent to the anode-facing surface of the cathode, and subsequently applying the polymer to trigger the crosslinking reaction that produces a usable conformal separator. Both the crosslinking agent and the polymer may be applied to the cathode either before or after installation of the cathode within the cell. Alternatively, the crosslinking agent and polymer may be premixed before being applied to the cathode. Again, the premixed compound may be applied to the cathode either before or after installation of the cathode within the cell. In accordance with one embodiment, the polymer is in the form of polyvinyl alcohol preferably having an average molecular weight greater than 13,000 and less than 500,000. In accordance with another embodiment, the weight ratio between the borate derivative and the vinyl alcohol is preferably between 1:1000 and 1:1.

[0029] In accordance with another embodiment, the borate derivative is boric acid that is combined with a polymer, such as polyvinyl alcohol. The resulting mixture is further combined with a base solution electrolyte, such as KOH to trigger the crosslinking reaction. The use of boric acid may be desirable in some instances as it may be premixed with the polymer (e.g., PVA) to form a non-reacting mixture, and subsequently sprayed onto the anode-facing surface of the cathode. The cathode may either be pre-wetted with electrolyte to immediately commence the crosslinking reaction, or the

electrolyte may be added after the mixture is applied to the cathode. It should further be appreciated that the mixture may be applied to the cathode either before or after installation of the cathode, and that the cathode may be pre-wetted either before or after installation of the cathode. Of course, the boric acid may be applied to the cathode separate from the polymer if desired. While a boric acid is used in accordance with this embodiment, it should be appreciated that the properties that allow it to cross-link the alcohol are inherent to other compounds falling under the general designation of a Lewis acid, which have an affinity for lone pairs of electrons. Because PVA is an electron donor, it binds in the presence of borate. Electron donors such as PVA are recognized as Lewis bases. While Boron-based compounds and PVA are used in accordance with the preferred embodiment, it should be appreciated that alternative Lewis acids and Lewis bases may be used to provide a conformal separator having the advantages associated with the present invention, borate and PVA being included within their respective genus.

[0030] A large variety of polyvinyl alcohol polymers may be used in the preferred embodiment of this invention including but not limited to those described in US patent #5,057,570, which is hereby incorporated by reference, and those sold by Celanese Chemicals. The weight average molecular weights of the employed polymers may be narrowly distributed, broadly distributed or bimodally distributed. Other polymers, such as guar gum and guar gum derivatives, copolymers of polyvinyl alcohol, or other polymeric materials with hydroxyl functional groups may be used in place of the polyvinyl alcohol and crosslinked with borate derivatives, including borate, boric acid and derivatives thereof, and boric acid esters (also named in IUPAC convention system as trialkyloxyboranes and triaryloxyboranes) including also cyclic boric acid esters and such borate esters as DeCORE BE-85 sold by DeForest Enterprises in Boca Raton, FL or other inorganic ions, as appreciated by those having ordinary skill in the art.

[0031] When a borate ester is used, the borate will normally crosslink without the organic portion of the ester being incorporated as part of the crosslinked network following a complete hydrolysis of the starting borate ester. Accordingly, the product of the crosslink includes the borate and not the organic portion of the borate ester. In other cases, if the borate ester has the organic portion built into the crosslinked portion of the gel, the crosslinking occurs through the borate moiety. Accordingly, in both cases, the crosslinking agent is inorganic in accordance with the present invention.

[0032] It is also foreseen that commercially available PVA/boric acid derived products such as Celvol MH-82, MM-81, MM-51 and MM-14 can also be successfully applied as

chemical components in the present invention having particular economic and manufacturing advantages. Furthermore, the borate solution may alternatively be substituted by compounds that form borate in aqueous solutions, such as BCl_3 or other halogenated compounds. This resulting reaction produces a strong polymer gel matrix. It has been discovered that, surprisingly, when polyvinyl alcohol and borate solutions are applied to electrode elements, they form a thin, strong, stable and functional separator film 32. Moreover, because borate and polyvinyl alcohol are both safe to handle, the fabrication process is simplified compared to conventional separators. The resulting film 32 may be applied to the electrodes either prior to assembly or directly onto the electrodes that have been preinstalled into a cell, and pre-wetted with electrolyte (preferably KOH) prior to crimping.

[0033] In accordance with an alternate embodiment, the boric acid or other boron-based derivative and polyvinyl alcohol may be applied to the radially inner surface of a conventional non-woven fabric separator. The fabric adds structure to the separator fabricated in accordance with this alternate embodiment, absorbs additional electrolyte, and may be manufactured thinner than conventional non-woven fabric separators, thereby increasing the volume of active material in the cell. This embodiment can also reduce the resistance resulting from the separator component of the cell.

[0034] In accordance with yet another alternate embodiment, a di-alcohol is mixed with a borate derivative (e.g., sodium borate, potassium borate, zinc borate) to produce a polymerization reaction that produces a network polymer suitable for use as a conformal separator. Alternatively, the di-alcohol could be mixed with boric acid to facilitate application of the material with the crosslinking reaction proceeding upon the solution coming into the presence of electrolyte of alkaline solution.

[0035] The separator 32 thus produced in accordance with all of the above embodiments has been found to be stable in electrolyte over a long period of time even at high temperatures. Furthermore, the separator 32 has a porosity that is sufficient to enable a high degree of ionic conductivity between anode 26 and cathode 24, and furthermore achieves electrical isolation between the electrodes. One skilled in the art would also recognize that the electrolyte could contain additives of various types for various purposes. Common additives would be of the variety used to suppress gas generation in the anode of the cell. Other additives to the electrolyte could include but would not be limited to chemical agents that promote or accelerate crosslinking as well as soluble or suspendable crosslinking agents.

[0036] Various considerations may be made in the construction and manufacturing of the invention. Deciding whether to apply a borate or a boric acid to the cell depends both upon the type of cell and the process used to manufacture it. Those cells that are manufactured in a process where the alkaline electrolyte can be placed into the cathode prior to separator application are amenable to use of boric acid as a crosslinking agent for the separator. Cells in which the cell design or manufacturing layout do not easily provide a means to get alkaline material into the cathode or onto its surface prior to application of the separator are candidates to use borates as crosslinking agents.

[0037] Other considerations regarding the best use of the invention include deciding when and how to apply the separator to the cathode. In those instances where the cathode is substantially assembled outside of the cell, as is often the case with zinc air cells, the application of the separator to the cathode may be done prior to the insertion of the cathode into the cell can. This certainly does not preclude the application of the separator after the cathode is inserted into the cell can but may offer significant advantages in cost and quality depending upon the manufacturing and process layouts. In those instances where there is significant handling of the cathode to get it properly installed into the cell can, as is often the case in cylindrical cell manufacturing, the separator is best applied after the cathode has been inserted into the cell can. Common cylindrical designs are also benefited by the application of the separator onto regions at the bottom of the cell can 20 where the separator functions to insulate the anode material from the cathode can wall.

[0038] While various embodiments of the present invention have been described above, several examples are presented below that further describe the fabrication and installation of the conformal separator constructed in accordance with the present invention in the cell. Again, unless otherwise stated, the examples below apply both to cylindrical and metal-air cells. Furthermore, while the percentages by weight of certain compounds are specified in accordance with the given examples, it should be appreciated that the PVA preferably has a concentration anywhere between 0.5% and 12%, and the borate preferably has a concentration up to 5% while remaining soluble in the PVA solution.

EXAMPLE 1

[0039] To produce the separator 32 in accordance with one embodiment of the invention, a sufficient amount of polyvinyl alcohol, such as CELvol 350, commercially available from Celanese Chemicals, Inc. located in Dallas, TX, is dissolved in water and heated to produce a 2% solution, and subsequently cooled to room temperature. A 5% sodium

borate solution is sprayed or otherwise applied onto the surface of the cathode at a location that will ultimately define the interface between cathode and anode when the cathode is installed into the cell. The polyvinyl alcohol solution is subsequently spread onto the inner surface of the cathode using, for example, an acrylic rod, and is crosslinked via the sodium borate. The cathodes are then allowed to dry before being inserted into the cell. Alternatively, the sodium borate and polyvinyl alcohol solutions may be applied to the cathodes after insertion into the cell.

[0040] One significant function of separator 32 is to maintain electrical isolation between the anode 26 and cathode 24. Otherwise, the resulting short circuit will cause the open circuit voltage (OCV) of the cell to decrease rapidly, thereby causing the cell to fail prematurely. OCV values were determined for 13A size zinc air cells having a conformal separator constructed in accordance with the present embodiment and compared against a control group of cells having a traditional separator made of non-woven fabric. The results, illustrated in Table 1, demonstrate the reliable and durable electrical separation of the electrodes in cells that include the conformal separator at room temperature as well as elevated temperatures. In fact, under elevated temperatures, the cells containing the conformal separator achieved greater electrical isolation than the control group, as evidenced by the reduced number of cells that failed.

TABLE 1

CELL TYPE	4 weeks at 21° C		4 weeks at 60° C	
	OCV	No. failed cells	OCV	No. failed cells
Control	1.260	0	1.216	8
Conformal separator	1.255	0	1.228	1

[0041] A cell's discharge capacity provides yet another indication of a cell's performance. In particular, if the separator 32 does not provide sufficient ionic conduction between the electrodes 24 and 26, the cell will fail prematurely during discharge. Discharge capacities were determined at 3 mA for 13A size zinc air cells having a traditional fabric separator, and 13A size zinc air cells having a conformal separator in accordance with the preferred embodiment. The results, illustrated in Table 2, demonstrate that the high discharge capacity associated with the cells having the conformal separator 32 provide sufficient ionic conduction between the electrodes 24 and 26. Accordingly, the electrochemical cell is able to completely discharge during use.

TABLE 2

CELL TYPE	DISCHARGE CAPACITY (mAh)
Control	269
Conformal Separator	274

Alternatively, the polymer (PVA) and crosslinking agent may be sprayed in an alternating manner onto the anode-facing surface of the cathode. In particular, the chemicals may be sprayed using a compact spray gun such as the Nordson MEG™ electric spray gun controlled by an EPC-15 system controller and pressurized with a CP high pressure pump all available from Nordson Corporation, located in Amherst, OH. It has been found that this system is able to spray at a rate of .001 g/cm², thereby producing a very fine layer of the compound being applied. The crosslinking agent and polymer may thus be iteratively sprayed until it a minimum necessary thickness is determined to ensure electrical isolation between the cell electrodes. The repetitious spraying thus enables the production of a conformal separator whose thickness is minimized while maintaining cell stability to maximize the cell contents and further adding to the life and performance of the cell.

EXAMPLE 2

[0042] The polyvinyl alcohol and sodium borate solutions described above with reference to Example 1 were applied to the inner surfaces of Rayovac D size alkaline cell cathodes that were inserted into the container 20 to provide a separator 32 in accordance with the preferred embodiment. The performance of the cells was compared to a control group alkaline cells of the same size having traditional fabric separators for their discharge capacity to 1.1 V at 1.4 A. The specific energy for the cells was also determined. Referring to Table 3, the LR20 cells including the conformal separator 32 provide a higher capacity than those having a fabric separator. Furthermore, the discharge voltage of the LR20 cells having the conformal separator 32 was greater, thereby contributing to the greater specific energy of these cells.

TABLE 3

CELL TYPE	DISCHARGE CAPACITY (Ah)	SPECIFIC ENERGY (Wh)
Control	1.27	1.50
Conformal Separator	1.62	1.95

EXAMPLE 3

[0043] A Rayovac size AA alkaline cell cathode that had been inserted into the container was pre-wetted with 0.8 g of 37% KOH electrolyte solution. A 2% by weight solution of Celvol MH-81 consisting of a bimodal weight average molecular weight distribution hydrated polyvinyl alcohol and boric acid (PVA/BA) was prepared following the manufacturer's recommended procedure. In particular, MH-81 is purchased in solid form, and subsequently mixed with water to prepare a solution. Because the boric acid requires KOH to encourage the crosslinking reaction, the PVA/BA mixture is relatively easy to apply to the cell cathodes. In particular, The PVA/BA solution was applied to the inner surfaces of Rayovac size AA alkaline cell cathodes that had been pre-inserted into the container, and thus pre-wetted with KOH, to provide a conformal separator in accordance with the present invention. The performance of the cells was compared to a control group of alkaline cells having traditional fabric separators. The discharge voltage of the cells having the conformal separator was greater, thereby contributing to the greater specific energy of these cells.

EXAMPLE 4

[0044] A Rayovac LR06 alkaline cell cathodes that had been inserted into the container was pre-wetted with 0.8 g of 37% KOH electrolyte solution. A 2% by weight solution of Celvol MH-82 polyvinyl alcohol/boric acid (PVA/BA) was prepared following the manufacturer's recommended procedure. Using an air-propelled spray system the PAV/BA solution was sprayed onto the inner surfaces of Rayovac LR06 alkaline cell cathodes that had been pre-inserted into the container and wetted with electrolyte. The reaction of the boric acid with KOH initiated crosslinking of the PVA in order to provide a conformal separator in accordance with the preferred embodiment.

EXAMPLE 5

[0045] A separator in accordance with another embodiment of the present invention is produced by applying thin layers of conformal separator to the surface of a traditional non-woven fabric, however, the fabric used in accordance with the present method has a thickness (approximately .13 mm) less than that suitable to provide a conventional separator (approximately .26 mm). A skilled artisan appreciates that conventional separators include at least four wrappings of non-woven fabric in order to provide

electrical isolation that is adequate to render the separator suitable in an electrochemical cell. The present embodiment uses a double wrap (or optionally a single wrap) of non-woven fabric that is treated with a conformal separator of the present invention.

[0046] In particular, a solution containing 0.012 g of polyvinyl alcohol (PVA) and boric acid (BA) was applied to the inner surfaces of a double wrap of conventional non-woven fabric separator having a surface area of 11.7 cm². The fabric had been pre-inserted within a Rayovac size AA alkaline cell cathodes that had previously been inserted into the container and pre-wetted with electrolyte.

[0047] The solution was applied by spraying using a compact spray gun such as the Nordson MEG™ electric spray gun controlled by an EPC-15 system controller and pressurized with a CP high pressure pump all available from Nordson Corporation, located in Amherst, OH. Successful applications were obtained only upon precise orientation of the spray gun head position, the can/cathode/fabric assembly position, can/cathode assembly rotation, spray pattern and spray duration. Useful regions to obtain uniform coverage of the interior wall of the fabric were obtained below 600 psig of fluid pressure pumping through nozzle heads commercially identified as .02-2, .04-2 and .06-2 nozzle heads using application time of less than 1 second and as low as 0.01 seconds. Can rotations of 600 rpm and greater were also helpful in maintaining an even coating of the solution onto the substrate. Because the thickness of the crosslinking products is less than .13 mm (the thickness of two additional wraps of non-woven fabric), the resulting conformal separator has the stability of the non-woven fabric while creating additional room within the cell for active material than previously achieved using non-woven fabric separators, thereby enhancing the life and performance of the cell.

[0048] The present invention recognizes that PVA could be applied directly to the non-woven fabric to produce a useful separator. However, the present embodiment advantageously adds an inorganic crosslinking agent to the PVA to render the separator more robust and physically stable than a combination of PVA and non-woven fabric alone. It is believed that the higher molecular weight of the present embodiment in combination with the crosslinking of the PVA produces the higher strength and stability of the present separator.

[0049] Referring now to Fig. 3, the performance of these size AA cells was compared to a control group of alkaline cells having traditional fabric separators. In particular, cells were discharged at 1 Amp constant current. Those cells containing the separator of the present embodiment of the invention discharged at a higher voltage and lasted a longer

period of time before reaching 1.1, 1.0 and 0.9 volt cut-offs. Furthermore, the discharge voltage of the size AA cells having the conformal separator was greater, thereby contributing to the greater specific energy of these cells.

[0050] It should alternatively be appreciated that the PVA and boric acid may be applied to the fabric prior to insertion of the separator into the cell, it being appreciated that the crosslinking will occur upon the addition of electrolyte. The performance of two size "AA" cells constructed in accordance with this embodiment were tested against a control group of alkaline cells. Those cells containing the separator constructed by applying PVA and boric acid to the fabric prior to insertion of the separator into the cell discharged at a slightly higher voltage and lasted a significantly longer period of time than the control group. Furthermore, the discharge voltage of the size AA cells having this conformal separator was greater.

ALTERNATE EMBODIMENTS

[0051] While the above examples for fabricating zinc air and alkaline cells incorporating the conformal separator 32 have been described in accordance with the preferred embodiment, the present invention includes alternate embodiments that can enhance the functionality of separator 32. In particular, inorganic ions such as potassium and calcium may be crosslinked with carrageenan and other organic polymers to provide a conformal separator in accordance with the present invention. Even though carrageenan is organic, this fabrication improves upon conventional methods by employing an inorganic crosslinking agent, thereby rendering the fabrication process less hazardous and, consequently, more efficient.

[0052] Additionally, structural and/or absorbent filler materials may be added to the conformal separator to provide additional structure and to absorb additional electrolyte, thereby increasing the conductivity of the cell. Examples of absorbent filler materials include polyvinyl alcohol fibers and cellulose fibers, which are also structural materials, while strictly structural filler materials may comprise polymer fibers or other inorganic powders. Pore forming materials, such as zinc oxide and barium sulfate, may be further added to the separator. The pore forming materials react with the electrolyte to produce apertures in the separator that are sufficiently small so as to maintain electrical isolation between the anode and cathode while increasing the conductivity of the cell.

[0053] The ionic conductivity of the separator 32 may be further increased by combining the polyvinyl alcohol and borate with anion conducting materials, such as a hydroxide

ion, and anion exchange polymers, for example cationic quaternary ammonium ion polymers. These anion conducting materials may assume the form of solid resins, soluble polymers, and polymers copolymerized with the materials that comprise the conformal separator. Conductivity may further be enhanced by adding cationic compounds to the electrode, conformal separator materials, or the electrolyte. For examples, quaternary ammonium ions may be mixed with polyvinyl alcohol, the boric acid, or applied directly to the battery electrode or added to the electrolyte. Conductivity may further be increased by the addition of inorganic materials such as laponite, bentonite or smectite clays, or clay-like materials. Finally, the conductivity may be enhanced by adding inorganic or organic salts, including metal hydroxide salts, into the separator 32. If the salt is soluble, additional pores will be formed in the separator to increase electrolyte flow as described above. If the salt is insoluble, the conductivity of the separator will be increased, as appreciated by those having ordinary skill in the art. The hydroxide salt may be mixed with the polyvinyl alcohol, the borate crosslinking solution, or applied directly to the electrode or added to the electrolyte.

[0054] The invention has been described in connection with what are presently considered to be the most practical and preferred embodiments. However, the present invention has been presented by way of illustration and is not intended to be limited to the disclosed embodiments. Accordingly, those skilled in the art will realize that the invention is intended to encompass all modifications and alternative arrangements included within the spirit and scope of the invention, as set forth by the appended claims.

Industrial Applicability

The present invention provides conformal separators that prevent electrical contact between the electrodes of electrochemical cells while permitting electrolyte transfer therebetween.

CLAIMS

WE CLAIM

1. An electrochemical cell comprising:
a container;
a cathode material disposed in the container and presenting an anode-facing surface;
an anode material disposed in the container adjacent the anode-facing surface; and
a conformal separator disposed between the anode-facing surface of the cathode and the anode, wherein the separator prohibits electrical contact between the anode and cathode while permitting electrolyte transfer between the anode and cathode, the separator being formed from a polymer and an inorganic crosslinking agent.
2. The electrochemical cell as recited in claim 1, wherein the crosslinking agent comprises a borate derivative.
3. The electrochemical cell as recited in claim 2, wherein the borate derivative is selected from the group consisting of potassium borate, sodium borate, zinc borate, and boric acid.
4. The electrochemical cell as recited in claim 3, wherein the borate derivative is boric acid.
5. The electrochemical cell as recited in claim 4, wherein the borate derivative is mixed with the polymer and electrolyte.
6. The electrochemical cell as recited in claim 1, wherein the polymer comprises a plurality of hydroxyl groups.
7. The electrochemical cell as recited in claim 6, wherein the polymer is a vinyl alcohol.
8. The electrochemical cell as recited in claim 7, wherein the polymer comprises polyvinyl alcohol.

9. The electrochemical cell as recited in claim 8, wherein the polyvinyl alcohol has an average molecular weight greater than 13,000 and less than 500,000.
10. The electrochemical cell as recited in claim 1, wherein the cell is selected from the group consisting of a cylindrical cell and a metal-air cell.
11. The cell as recited in claim 1, wherein the separator further comprises a non-woven fabric having at least one of an inner surface that faces the anode when installed within the cell and an outer surface that faces the cathode when installed within the cell, further comprising a crosslinked polymer disposed on a surface selected from the inner surface and the outer surface.
12. The electrochemical cell as recited in claim 1, wherein the polymer comprises a di-alcohol.
13. The electrochemical cell as recited in claim 1, wherein the polymer is selected from the group consisting of guar gum, guar gum derivatives, copolymers of polyvinyl alcohol, and polymeric materials with hydroxyl functional groups.
14. The electrochemical cell as recited in claim 1, wherein the polymer comprises polyvinyl alcohol and the crosslinking agent comprises a borate derivative, and wherein the weight ratio between the borate derivative and the vinyl alcohol is between 1:1000 and 1:1.
15. The electrochemical cell as recited in claim 1, wherein the crosslinking agent is a Lewis acid, and wherein the polymer is a Lewis base.
16. An electrochemical cell comprising:
 - a container;
 - a cathode material disposed in the container having a surface that at least partially defines a void within the cell;
 - an anode material disposed in the container and at least partially occupying the void; and
 - a conformal separator disposed between the cathode surface and anode, wherein the separator prohibits electrical contact between the anode and cathode while permitting electrolyte transfer between the anode and cathode, the separator being formed from a polymer and a borate-derivative crosslinking agent.

17. The electrochemical cell as recited in claim 16, wherein the crosslinking agent comprises a borate ester.
18. The electrochemical cell as recited in claim 17, wherein the borate ester is selected from the group consisting of boric acid esters, cyclic boric acid esters, and DeCORE BE-85.
19. The electrochemical cell as recited in claim 16, wherein the polymer is selected from the group consisting of alcohol, guar gum, guar gum derivatives, copolymers of polyvinyl alcohol, and polymeric materials with hydroxyl functional groups.
20. The electrochemical cell as recited in claim 19, wherein the polymer comprises polyvinyl alcohol.
21. The electrochemical cell as recited in claim 16, wherein the cell is selected from the group consisting of a cylindrical cell and a metal-air cell.
22. A method of preparing a conformal separator for an electrochemical cell defining an enclosure, the steps comprising:
 - (a) installing a cathode within the enclosure, the cathode presenting an anode-facing surface;
 - (b) installing an anode within the enclosure, wherein anode is disposed adjacent the anode-facing surface;
 - (c) crosslinking a polymer with an inorganic crosslinking agent to form a compound; and
 - (d) applying the compound to the anode-facing surface, wherein the compound prevents electrical contact between the anode and cathode while permitting electrolyte transfer between the anode and cathode.
23. The method as recited in claim 22, wherein the crosslinking agent is a borate derivative, and wherein the polymer is a vinyl alcohol.
24. The method as recited in claim 23, wherein the compound is applied to the anode-facing surface prior to installing the cathode within the enclosure.
25. The method as recited in claim 23, wherein the compound is applied to the anode-facing surface after installing the cathode within the enclosure.

26. The method as recited in claim 23, wherein the borate derivative is boric acid, and wherein step (c) further comprising adding a base solution to the cathode.
27. The method as recited in claim 26, wherein the cathode is wetted with the base solution prior to step (d).
28. The method as recited in step 26, wherein the cathode is wetted with the base solution after step (d).
29. A method of preparing a conformal separator for an electrochemical cell defining an enclosure, the steps comprising:
- (a) installing a cathode within the enclosure, the cathode presenting an anode-facing surface;
 - (b) installing an anode within the enclosure, wherein anode is disposed adjacent the anode-facing surface;
 - (c) applying an inorganic crosslinking agent to the cathode at an interface between the cathode and the anode; and
 - (d) subsequently applying a polymer to the anode-facing surface of the cathode to form a crosslinked polymer, wherein the crosslinked polymer prevents electrical contact between the anode and cathode while permitting electrolyte transfer between the anode and cathode.
30. The method as recited in claim 29, wherein step (c) is performed prior to step (a).
31. The method as recited in claim 29, wherein step (c) is performed after step (a).
32. The method as recited in claim 29, wherein the crosslinking agent is a borate derivative.
33. The method as recited in claim 32, wherein the borate derivative is selected from the group consisting of sodium borate, potassium borate, zinc borate, and boric acid.
34. The method as recited in claim 33, wherein the crosslinking agent is boric acid, further comprising adding a base solution to the cathode.
35. The method as recited in claim 34, wherein the base solution is added prior to step (a).

36. The method as recited in step 35, wherein the base solution is added after step (a).
37. A method of preparing a conformal separator for an electrochemical cell having an anode and a cathode, the steps comprising:
- (a) installing a cathode within the enclosure, the cathode presenting an anode-facing surface;
 - (b) installing an anode within the enclosure, wherein anode is disposed adjacent the anode-facing surface;
 - (c) applying a solution containing a polymer and an inorganic crosslinking agent onto the anode-facing surface of the cathode at an interface between the anode; and
 - (d) reacting at least one of the polymer and crosslinking with a constituent of the electrolyte solution to cause the formation of a separator compound at the anode-facing surface, wherein the compound prevents electrical contact between the anode and cathode while permitting electrolyte transfer between the anode and cathode.
38. The method as recited in claim 37, wherein step (c) further comprises spraying the solution onto the anode-facing surface.
39. The method as recited in claim 37, wherein the constituent comprises a base solution.
40. The method as recited in claim 39, wherein the constituent comprises KOH.
41. The method as recited in claim 37, wherein the constituent of the electrolyte solution is added to the cathode prior to step (c).
42. The method as recited in claim 37, wherein the constituent of the electrolyte solution is added to the cathode after step (c).
43. The method as recited in claim 37, wherein the cathode is installed in the cell prior to step (c).
44. The method as recited in claim 37, wherein the cathode is installed in the cell after step (c).

45. A method of preparing a conformal separator for an electrochemical cell having an anode and a cathode, the steps comprising:

- (a) installing a cathode within the enclosure, the cathode presenting an anode-facing surface;
- (b) installing an anode within the enclosure, wherein anode is disposed adjacent the anode-facing surface;
- (c) applying a crosslinking agent to the anode-facing surface of the cathode; and
- (d) after step (c), spraying a crosslinkable polymer on the anode-facing surface of the cathode to form a crosslinked polymer; and
- (e) repeating steps (c) and (d) at least once to build up a compound that prevents electrical contact between the anode and cathode while permitting electrolyte transfer between the anode and cathode.

46. The method as recited in claim 45, wherein the crosslinking agent is inorganic.

47. The method as recited in claim 46, wherein the crosslinking agent is a borate derivative.

48. The method as recited in claim 45, wherein the polymer comprises an alcohol.

48. The method as recited in claim 45, wherein step (c) occurs before step (a).

49. The method as recited in claim 45, wherein step (c) occurs after step (a).

50. A method of preparing a non-woven fabric separator having a crosslinked polymer disposed on its surface for an electrochemical cell, the steps comprising:

- (a) applying an inorganic crosslinking agent to the surface of the paper; and
- (b) subsequently applying a crosslinkable polymer to the surface of the separator to form a crosslinked polymer, wherein the compound prevents electrical contact between the anode and the cathode during cell use.

51. The method as recited in claim 50, wherein the non-woven fabric has a thickness not greater than .13 mm.

52. The method as recited in claim 50, further comprising the steps of installing the treated separator in an electrochemical cell after step (b) and subsequently applying an alkaline solution to cause the polymer to crosslink in the presence of the crosslinking agent.

53. The method as recited in claim 50, further comprising the steps of installing the non-woven fabric in an electrochemical cell prior to step (a) and applying an alkaline solution to the separator after step (b) to cause the polymer to crosslink in the presence of the crosslinking agent.

2/4

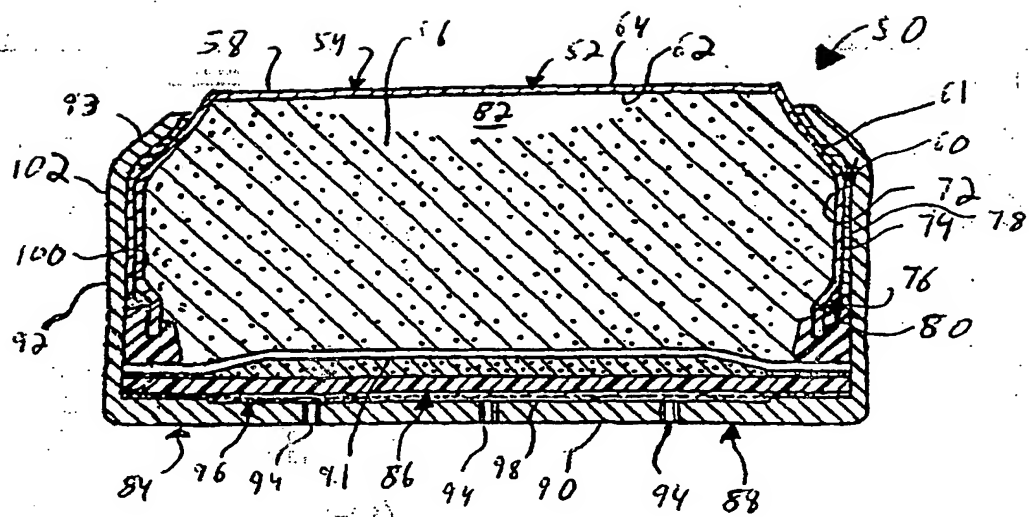
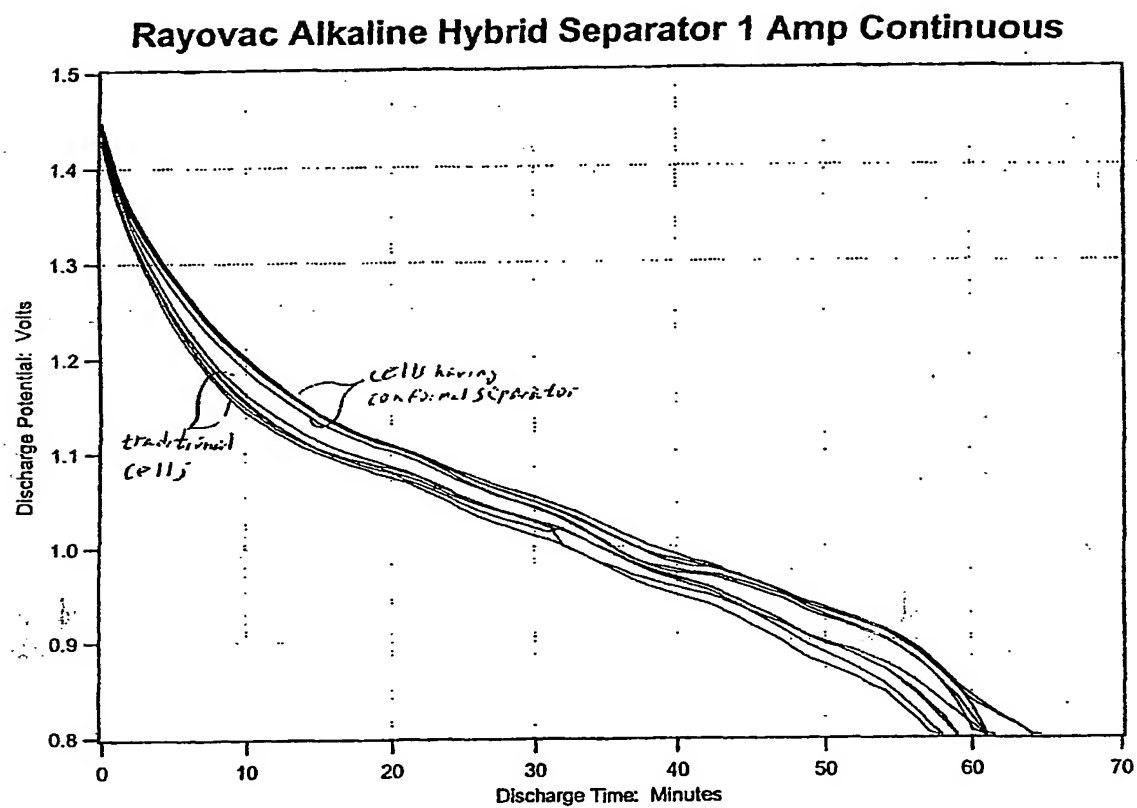


FIG 2

3/4

**FIG 3**

4/4

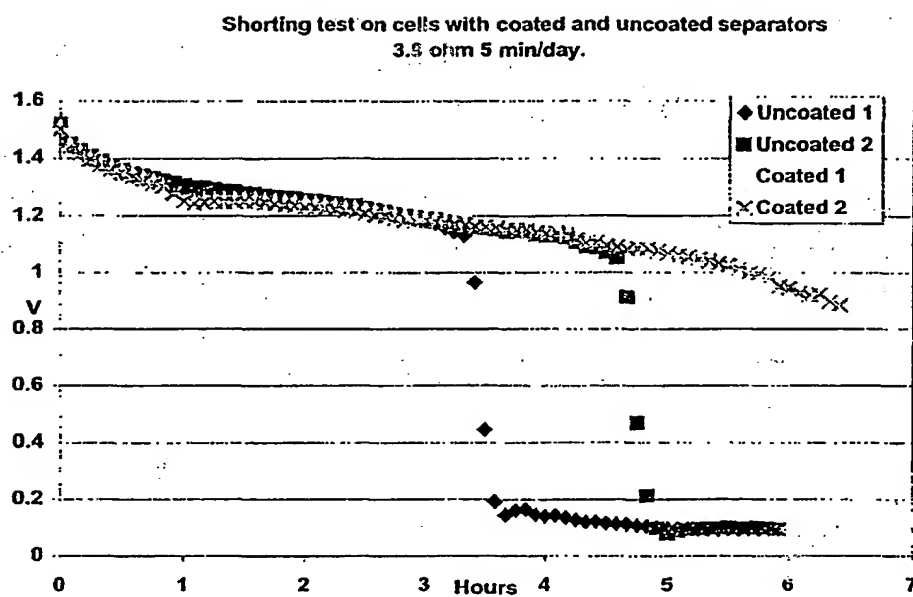


FIG 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/16823

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 02, 28 February 1997 (1997-02-28) & JP 08 273653 A (NIPPON OIL CO LTD), 18 October 1996 (1996-10-18)	1-3,5-8, 10,12, 13,15-23
Y	abstract	26,28
X	PATENT ABSTRACTS OF JAPAN vol. 004, no. 189 (E-039), 25 December 1980 (1980-12-25) & JP 55 130067 A (FURUKAWA ELECTRIC CO LTD;THE;OTHERS: 01), 8 October 1980 (1980-10-08)	1-9,12, 13,15-20
Y	abstract	14
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

12 September 2002

Date of mailing of the international search report

20/09/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Hintermaier, F

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/16823

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 037 033 A (TAKAMURA TSUTOMU ET AL) 19 July 1977 (1977-07-19) column 2, line 51 - line 66; figure 1 column 3, line 47 - line 63 -----	11
Y	US 4 361 632 A (WEBER ROBERT E ET AL) 30 November 1982 (1982-11-30) column 4, line 4 - line 63 column 5, line 51 - line 55 -----	14
X	JP 49 109834 A (MATSUSHITA) 18 October 1974 (1974-10-18) WPI/Derwent abstract -----	50-53
Y	EP 0 569 938 A (KURARAY CO ; JAPAN VILENE COMPANY (JP)) 18 November 1993 (1993-11-18) page 5, line 47 - line 51 -----	26, 28
X	WO 00 59052 A (GILLETTE CO ; TREGER JACK (US); ADAMSON DAVID V (US); CERVERA JAMES) 5 October 2000 (2000-10-05) page 3, line 8 - line 15 page 4, line 3 - line 23 page 5, line 5 - line 10 page 16, line 20 - line 32 page 18, line 7 - line 13 page 24, line 29 - line 31 -----	37-44

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/16823

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 08273653	A	18-10-1996	NONE	
JP 55130067	A	08-10-1980	NONE	
US 4037033	A	19-07-1977	JP 1087722 C JP 51083134 A JP 56026108 B CA 1060949 A1 DE 2601571 A1 FR 2298193 A1 GB 1530961 A	23-03-1982 21-07-1976 16-06-1981 21-08-1979 22-07-1976 13-08-1976 01-11-1978
US 4361632	A	30-11-1982	NONE	
JP 49109834	A	18-10-1974	JP 882806 C JP 52011008 B	30-09-1977 28-03-1977
EP 0569938	A	18-11-1993	DE 69301860 D1 DE 69301860 T2 EP 0569938 A1 JP 6029155 A	25-04-1996 01-08-1996 18-11-1993 04-02-1994
WO 0059052	A	05-10-2000	AU 4024800 A WO 0059052 A2 US 2001028976 A1	16-10-2000 05-10-2000 11-10-2001

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)